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## Doping and Electrochemical Capacitance of Carbon Nanotube-Polypyrrole Composite Films

Mark Hughes, George Z. Chen, Milo S. P. Shaffer, Derek J. Fray and Alan H. Windle  
Department of Materials Science and Metallurgy, University of Cambridge, Pembroke Street,  
Cambridge CB2 3QZ, UK.

### ABSTRACT

Composite films were electrochemically synthesised via the simultaneous deposition of multiwalled nanotubes and polypyrrole, a conducting polymer. Negatively charged functional groups attached to the surface of the acid treated nanotubes enables the tubes to act as a dopant for the PPY in these films. Scanning electron microscopy, cyclic voltammetry and electrochemical impedance spectroscopy revealed that the nano-porous three-dimensional arrangement of PPY coated MWNTs in these films produced specific capacitances per mass and geometric area as high as  $192 \text{ F g}^{-1}$  and  $1.0 \text{ F cm}^{-2}$ , respectively. This value of specific capacitance per geometric area exceeds that of both component materials and other carbon nanotube-conducting polymer composites. The composite films described in this report were also able to charge and discharge more than an order of magnitude faster than similarly prepared pure PPY films. The nano-porosity and small diffusion distances within the composite films, crucial to achieving the superior capacitive performance, were found to be dependent on the concentration of nanotubes and additional dopant anions in the polymerisation electrolyte, offering possibilities for tailoring of the composite structure.

### INTRODUCTION

Growing demands in industries such as transport and communication for electrical energy storage devices that can deliver high power level pulses have prompted considerable interest in electrochemical capacitors, or supercapacitors. While carbon nanotubes and conducting polymers have separately received considerable attention as supercapacitive materials, only recently has the capacitive performance of composites made by combining these two materials been reported, revealing capacitances greater than that of either component material.<sup>[1-4]</sup> Composites of carbon nanotubes and conducting polymers such as polypyrrole, polyaniline and poly(p-phenylene vinylene) can be grown by simply mixing the polymer and nanotubes,<sup>[5-7]</sup> or using a variety of chemical<sup>[8,9]</sup> and electrochemical<sup>[4,10-12]</sup> polymerisation techniques. The superior supercapacitive performance of carbon nanotube-conducting polymer composites is attributed to their nano-porous structure which combines the three-dimension charge storage capabilities of redox active conducting polymers, with the high surface area and electrical conductivity of carbon nanotubes. Here we report the supercapacitive properties of a particular carbon nanotube-polypyrrole composite in which the conducting polymer is doped by the embedded nanotubes.

### EXPERIMENTAL DETAILS

Multi-walled carbon nanotubes (MWNTs) and polypyrrole (PPy) were simultaneously deposited onto a graphite disk working electrode ( $0.33 \text{ cm}^2$ ) using an oxidising potential of 0.7 V measured against a saturated calomel reference electrode (SCE) in a three electrode, single

compartment cell.<sup>[1,10]</sup> The aqueous polymerisation electrolyte generally consisted of 0.5 M pyrrole monomer and 0.025 wt% to 0.4 wt% MWNTs (supplied by Hyperion). The MWNTs (outer tube diameter  $\sim 10$  nm; tube lengths from 0.2  $\mu\text{m}$  to 2.5  $\mu\text{m}$ ) were suspended in solution using a previously described acid treatment process which attaches hydroxyl, carbonyl and carboxylic groups to the tube surface, giving the MWNTs a net negative charge and enabling them to act as both a supporting electrolyte during polymerisation, and as a dopant in the PPY deposited on the working electrode.<sup>[1,10,13]</sup> The effect of adding additional dopants such as chloride ions and dodecyl sulphate ions to the polymerisation electrolyte in 0.01 M concentrations was also examined to determine the structural and electrochemical implications of using competing dopants in MWNT-PPY composites.

Once formed, composite films of various film-formation charges (a measure of the amount of film grown) were compared to similarly prepared pure PPY films ( $\text{Cl}^-$  doped) using cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) in an aqueous 0.5 M KCl electrolyte at potentials between  $-0.8$  and  $0.5$  V vs. SCE. CV analysis was performed on a model 273A EG&G Princeton Applied Research potentiostat and EIS studies were conducted using a Solartron 1260 impedance/gain-phase analyser coupled with a Solartron 1287 electrochemical interface employing a sine-wave amplitude of 10 mV and a frequency range of  $5 \times 10^5$  Hz to  $1 \times 10^{-2}$  Hz.

## RESULTS AND DISCUSSION

Figures 1 and 2 compare the CV and EIS results of MWNT-PPY composite films (aqueous polymerisation electrolyte: 0.5 M pyrrole and 0.4 wt% MWNTs) with similarly prepared pure PPY films (aqueous polymerisation electrolyte: 0.5 M pyrrole and 0.5 M KCl). The cyclic voltammograms (Figure 1a) indicate several important differences between the two films. The first of these is that the peak potentials of the composite film are about 200 mV more negative than those of the pure PPY film, confirming the anionic dopant role of the MWNTs.<sup>[1,10]</sup> The second point is that the output current of the composite film is about twice that of the pure polymer. Since capacitance is given by the output current divided by the scan rate, this implies that the capacitance of the composite films is about double that of the pure polymer.

The impedance plot shown in Figure 1b can be divided into a high frequency component (inclined at about  $45^\circ$ ) and a low frequency component (near vertical). The projected length of the high frequency Warburg-type line on the real axis ( $Z'$ ) characterises the slow ion migration process in the solution pores and is equal to one third the film's ionic resistance.<sup>[14]</sup> The composite and pure PPY films shown in Figure 1b had ionic resistances of  $0.8 \Omega$  and  $8.2 \Omega$ , respectively, indicating a lower barrier to ionic transport in the composite film. The superior ionic transfer of the composite films is even more exaggerated at bias potentials lower than 0.4 V.

The low frequency capacitance ( $C_f$ ) of the films produced was determined from the slope of a plot of the imaginary component of impedance ( $Z''$ ) at low frequency, versus the inverse of frequency ( $f$ ) using the equation  $C_f = (2\pi/Z'')^{-1}$ . Specific capacitances per mass and geometric area as high as  $192 \text{ F g}^{-1}$  and  $1.0 \text{ F cm}^{-2}$ , respectively were observed for the MWNT-PPY composite films. While the capacitance per mass of composite film is quite high, it is the capacitance per area of deposition surface that draws the most interest. This value is significantly larger than that reported for supercapacitors based on conducting polymers, carbon nanotubes or other carbon nanotube-conducting polymer composites.<sup>[2-4,15]</sup>

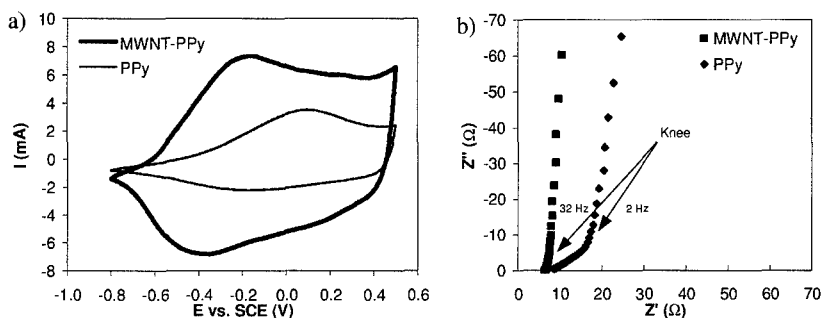


Figure 1. Comparison of MWNT-PPy composite films and pure PPy films prepared using similar conditions: a) cyclic voltammograms (film-formation charge:  $1.8 \text{ C cm}^{-2}$ , scan rate:  $50 \text{ mV s}^{-1}$ , electrolyte:  $0.5 \text{ M KCl}$ ); b) complex plane impedance plots (film-formation charge:  $1.0 \text{ C cm}^{-2}$ , bias potential:  $0.4 \text{ V vs. SCE}$ , electrolyte:  $0.5 \text{ M KCl}$ ).

Figure 2a shows how the low-frequency capacitance of the composite and pure PPy films increased with the film-formation charge. While the thickness of the composite and pure PPy films was found to increase approximately linearly with film-formation charge as expected<sup>[16]</sup> with slopes of  $3.5 \times 10^{-4} \text{ cm}^3 \text{ C}^{-1}$  and  $1.8 \times 10^{-4} \text{ cm}^3 \text{ C}^{-1}$ , respectively, their capacitance deviated from its initially linear relationship for large film-formation charges (Figure 2a). This deviation is attributed to limited electrolyte access at the lower levels of thick films. As a result, ion diffusion is not able to reach all the available PPy within the time frame of the capacitive measurements, thereby restricting the amount of material that can contribute to the measured capacitance, causing it to approach an upper limit with increasing film-formation charge.

The linear regions of the capacitance versus film-formation charge plots (Figure 2a) show that for a given charge, the composite film had a capacitance that was about double that of pure PPy, supporting the capacitive results obtained from the cyclic voltammograms. The slope ( $C/Q$ ) of these linear regions gives an indication as to the proportion of film that contributes to the capacitive performance. The superior slope of the composite films implies that more of the PPy in the film is able to access ionic charge from solution and hence contribute to the measured capacitance. The larger limiting value of capacitance apparent for the composite films indicates that their improved performance for a given polymerisation charge is not simply a result of an increase in polymerisation efficiency, which would result in the deposition of more polymer for a given polymerisation charge, relative to the pure PPy films.

The point that divides the high frequency component of the complex plane impedance plot from the low frequency component is referred to as the knee frequency<sup>[17]</sup> (Figure 1b). The knee frequency indicates the maximum frequency at which predominantly capacitive behaviour can be maintained and was more than an order of magnitude higher for the MWNT-PPy composite films than pure PPy films (Figure 2b). For low film-formation charges the knee frequency of the composite supercapacitors was as high as  $200 \text{ Hz}$ , however, as the film-formation charge was increased the knee frequency decreased rapidly as shown in Figure 2b. This performance limitation is a common phenomenon for devices based on conducting polymers and is simply related to the reduction in electrolyte access and increase in diffusion distance with film thickness.<sup>[18]</sup>

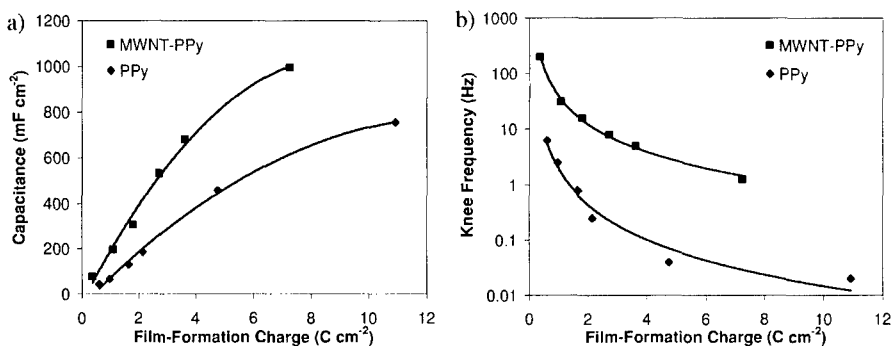


Figure 2. The relationship between film-formation charge and: a) low-frequency capacitance; b) knee frequency, for MWNT-PPy films and similarly prepared pure PPy films.

When dopant anions such as chloride ions and dodecyl sulphate ions were added to the polymerisation electrolyte, the porosity of the composite structures produced was significantly reduced as shown in Figure 3. These additional dopant ions facilitate PPy deposition in regions other than the negatively charged MWNT surfaces, enabling the PPy to fill inter-tubular voids, thereby reducing the size and number of nano-pores or eliminate them entirely. This blocking occurred both for chloride ions which are able to diffuse in and out of the PPy in response to redox cycling, and for large dodecyl sulphate ions which remain embedded in the PPy during redox cycling, necessitating the intercalation of charge balancing cations from solution. The decrease in electrolyte access and increase in diffusion distances associated with reduced nanoporosity lowered the film's capacitance by about 30% when chloride ions were added and more than 50% (to about that of pure PPy) when dodecyl sulphate ions were used, clearly illustrating the importance of the three-dimension network of nano-pores for low frequency capacitance. Additions of chloride ions and dodecyl sulphate ions were also observed to decrease the knee frequency by about 30%. It is interesting to note that even though the nano-pores were almost completely filled for films grown with added dodecyl sulphate, the knee frequency was still greater than that of pure PPy films, indicative of the improved ionic and electrical conductivity observed in the composite films relative to pure PPy films, particularly for low bias potentials.

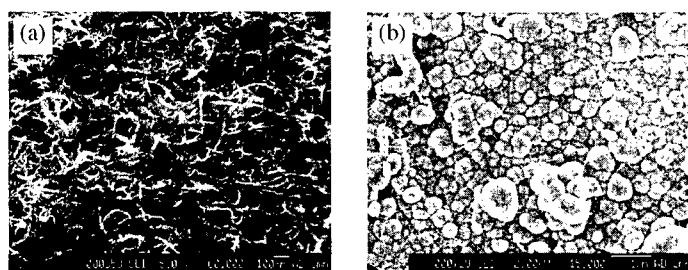


Figure 3. SEM images showing the reduction in porosity observed when using anionic dopants in addition to negatively charged MWNTs (film-formation charge: 1.8 C cm<sup>-2</sup>): a) mobile chloride ions; b) embedded dodecyl sulphate ions.

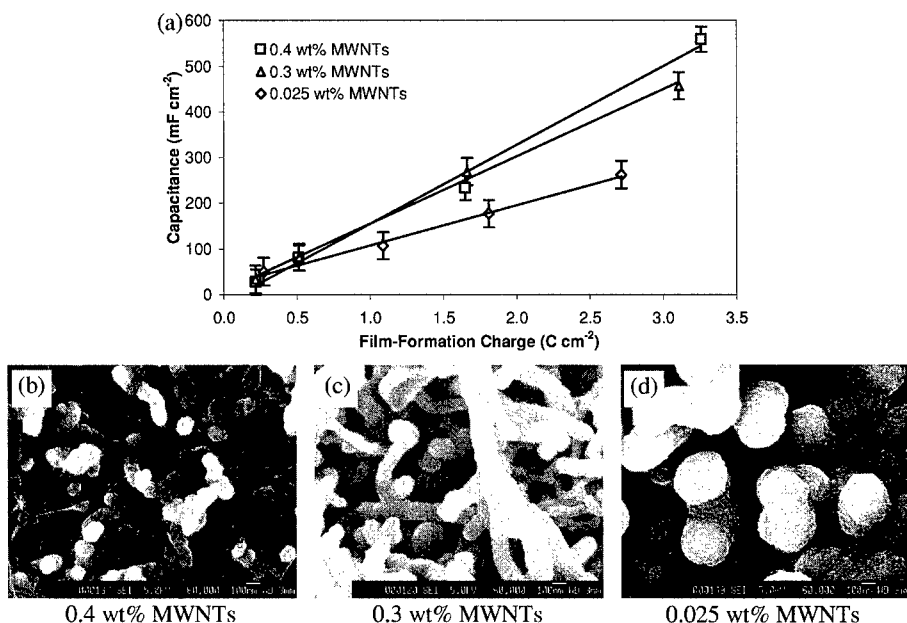


Figure 4. The effect of MWNT concentration in the polymerisation electrolyte on (a) specific capacitance (EIS electrolyte: 0.5 M KCl) and PPy coating thickness (film-formation charge < 1.8 C cm<sup>-2</sup>): (b) 40 nm for 0.4 wt% MWNTs; (c) 60 nm for 0.3 wt% MWNTs and (d) 160 nm for 0.025 wt%.

Figure 4 shows that as the concentration of MWNTs in the polymerisation electrolyte was decreased from 0.4 wt% to 0.025 wt%, while keeping the other growth conditions constant, the thickness of PPy coated onto each nanotube increased approximately linearly from 40 nm to 160 nm. As expected, the increase in PPy thickness, and hence diffusion distance, with decreasing MWNT concentration in the polymerisation electrolyte was associated with a reduction in specific capacitance for a given film-formation charge (Figure 4a). The relationship between polymer coating thickness and specific capacitance was also approximately linear and further illustrates the importance of reduced diffusion distances in the nano-porous structure.

## CONCLUSIONS

The nano-porous composites of negatively charged MWNTs and PPy produced in this report were capable of achieving specific capacitances per mass and geometric area as high as 192 F g<sup>-1</sup> and 1.0 F cm<sup>-2</sup>, respectively. This value is about double that of similarly prepared pure PPy films and is accompanied by more than an order of magnitude improvement in the rate of response relative to the pure polymer. These improvements represent a significant step towards fabrication of commercially applicable electrode materials. The superior capacitive performance of these films is closely linked with their nano-porosity and small diffusion lengths, properties that are

promoted by using high MWNT concentrations in the polymerisation electrolyte. Conversely, these structural aspects can be diminished by the introduction of additional doping anions, such as chloride and dodecyl sulphate ions. While the use of additional dopants to produce fully solid films may not be desirable for capacitor applications, these structures may find use in other devices, such as actuators, where excessive porosity may detract from the magnitude of response.

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